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THE ROLE OF FLY ASH IN CATALYTIC OXIDATION OF
S(IV) SLURRIES

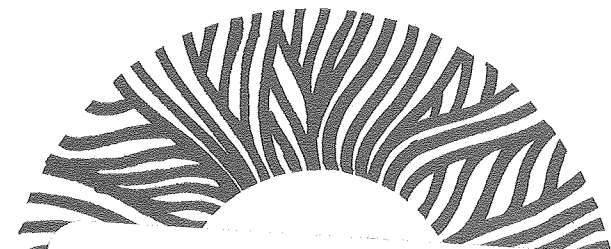
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THE ROLE OF FLY ASH IN CATALYTIC OXIDATION OF S(IV) SLURRIES

Sidney Cohen, Shih-Ger Chang, Samuel S. Markowitz, and Tihomir Novakov

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

The rate of catalytic oxidation of S(IV) in aqueous fly ash slurries has been examined by monitoring loss of SO_3^{2-} and O_2 , and SO_4^{2-} formation. Evidence from both filtering and extraction studies indicates that dissolved iron which has been leached from the ash is the chief catalyst. This homogeneous reaction dominates any catalytic effect of the ash surface.

Introduction

The catalytic behavior of fly ash in the oxidation of S(IV) in aqueous systems has been reported.¹⁻³ Prior work has considered the potential of fly ash as a scrubber medium,^{2,4} and suggested how fly ash may function in promoting acid rain formation in droplets.³ Although several properties of the ash — surface characteristics, metal oxide content, trace metal dissolution — have been proposed to account for its catalytic role, no systematic investigation of the nature of the catalysis has been made. It is important to distinguish between surface and homogeneous catalysis — for example, presence of chelating agents in wet scrubbers containing fly ash should inhibit catalysis by leached metals.^{1,5}

In this study the oxidation of S(IV) in slurries of fly ash has been examined after different ash pretreatment and under varying experimental conditions. Our evidence indicates that dissolved iron is a prime factor in fly ash catalyzed oxidation of SO₂.

Experimental

Reagents. Mallinckrodt or Baker reagent grade chemicals were used without further purification. The fly ash types were NBS Standard Reference Material 1433a and four lot samples, referred to as A-D. A is from the TVA Shawnee Power Plant; B, the Duke Power Steam Plant; C, the Jim Bridger Plant, Wyoming; and D, an untreated ash sample obtained from Lawrence Livermore Laboratory. Nanopure water from a Barnstead Deionizer was used throughout.

S(IV) oxidation. The net reaction being studied was $\text{HSO}_3^- + 1/2 \text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+$. The proportional quantities of HSO_3^- , $\text{SO}_2 \cdot \text{H}_2\text{O}$, and SO_3^{2-} vary with pH, so knowledge of the working pH is essential. Unless otherwise stated, the reaction pH was 3.1 ± 0.1 . Reactions were monitored using three different methods:

1. In open-air Erlenmeyer flasks agitated with a magnetic stirrer, S(IV) loss being monitored by iodometry.

2. Reaction set-up as above, except SO_3^{2-} loss and SO_4^{2-} appearance monitored by ion chromatography.

3. In a closed system — allowing no diffusion of O_2 into solution during the course of the reaction — with O_2 decay from initially saturated solutions being monitored with a Clark-type oxygen electrode.

The initial S(IV) concentration in the reactions studied varied from 9.0×10^{-4} to 1.5×10^{-2} M. The pH was varied from 2.5 to 3.9 by using appropriate mixtures of $\text{SO}_2 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_5$. The fly ash concentration was varied from 0.10% to 0.36% by weight.

Most rates reported are the average of 2-3 runs agreeing within 10%.

Leaching experiments. All glassware and containers were acid washed before use and rinsed 5 to 6 times with deionized water. Leachate solutions were stored in Nalgene linear polyethylene containers prior to analysis. For the leaching experiments, 2 grams of ash were suspended in 100 ml of the appropriate solvent and subjected to 20 min of ultrasonic agitation. In the $\text{NH}_2\text{OH} \cdot \text{HCl}$ extraction, the solutions were shaken over a period of 2 hr while pH equilibration occurred. The duration of treatment for the other solutions was chosen after a separate set of experiments revealed that soluble surface-associated species (SO_4^{2-} , CaO , As_2O_3) are almost entirely removed after only 5-10 min of treatment. Longer treatment periods in dilute (0.02 N) acid slowly solubilizes the matrix species (Fe, Al, Si), indicating breakdown of the aluminosilicate framework. Concentrations of the leaching solutions were as follows. Acid concentrations varied from 0.02 M to 1.8 M. HCl , H_2SO_4 , and HNO_3 all affected the ash reactivity similarly, indicating there is no anion or concentration effect within the bounds studied. Base concentrations were

either 0.05 M or 1.5 M NaOH. The $\text{NH}_2\text{OH}\cdot\text{HCl}$ concentration was 0.1 M and the pH was adjusted to 2.9. When extracted ash was to be used in subsequent experiments, it was dried at room temperature, then stored in sealed containers.

Equipment and materials. Elemental and chemical compositions of fly ash were characterized by X-ray fluorescence (XRF), atomic absorption (AA), and electron spectroscopy for chemical analysis (ESCA). AA work was performed on a Perkin-Elmer Model 360 atomic absorption instrument. The XRF procedure designed to minimize matrix and particle-size effects, has been described elsewhere.⁶ A 0.22- μm pore size Millipore filter was used to filter solutions for leachate analysis and reaction aliquots. This pore size was chosen as the maximum size which appears to trap all ash particles to which metals might absorb.⁷ ESCA work was done on an AEI ES200 instrument with an Al anode. A position-sensitive photoelectron detector was installed in our lab. Samples were mounted on the probe with double-backed sticky tape. Binding energies were referenced to the hydrocarbon C(1s) peak at 284.5 eV. Peak growth could be monitored continuously on a real time display and plotted when the signal-to-noise ratio was deemed sufficient. The analytical lines used for Fe and Mn were the $2\text{P}_{1/2}/2\text{P}_{3/2}$ doublets.

Results and Discussion

Care was taken to measure the true reaction rate, unrestricted by O_2 mass transfer into solution. The results described here underscore the need for such caution. For the S(IV) concentration range from 2×10^{-2} M down to 4×10^{-4} M, reaction curves were consistent with zeroth order dependence on [S(IV)] when reactions were run in open-air Erlenmeyer flasks (i.e., plots of [S(IV)] vs. time were linear). Correlation coefficients on the straight-line fits were generally 0.98 or higher. Some tailing was observed at the lowest concentrations.

It has been noted that mass transfer of O_2 into solution can be rate limiting for S(IV) consumption in the range of our experiments.⁸ Use of a fritted glass gas-dispersion bubbler to ensure air saturation effected no significant rate change compared to a similar run using only the magnetic stirrer. However, the zeroth order dependence described above, coupled with almost identical rates being observed for the four most active ash types (Table I), prompted further consideration of this problem. SO_2 evolution or precipitation of $CaSO_3$ could conceivably provide a S(IV) rate loss mimicking zeroth order rate behavior. Ion chromatography work, showing material balance between SO_3^{2-} lost and SO_4^{2-} formed, eliminated this possibility.

To avoid entirely the problem of O_2 saturation, the oxygen electrode monitoring system described in the experimental section was used. The rates, which slowed as the reaction proceeded, were extrapolated to zero time in order to make them representative of the reaction rate in an air-saturated solution. Table I shows that this clearly defines a reactivity scale for the ashes and increases rates for all but ash type B. The rate increase indicates that mass transfer of oxygen had previously been a problem. The slower rate for ash type B is not surprising because initial rates (first 3-4 minutes of reaction) were generally slower regardless of the monitoring set-up used. This phenomenon will be discussed more fully below.

Role of surface in catalysis. To determine the relative importance of surface-mediated or solution-phase reactions, a reaction slurry was filtered after the reaction was partially complete. Loss of sulfite was monitored in the filtrate; as can be seen in Fig. 1, the reaction rate is not affected by removing particulate matter.

Because the catalysis is apparently due to trace metals which can be leached from the ash, an attempt was made to remove such species from the ash

surface by leaching with different solvents. Leaching with deionized water or strongly basic solution did not affect the ash reactivity. However, an acid wash in 0.02 N acid completely deactivated the ash. Metals commonly implicated in SO_2 oxidation — Cu, Fe, Mn, Co, V — can be wholly or partially removed by an acid wash (depending on their chemical state), so it is not surprising that washing with acid deactivates the fly ash.

Identification of catalytic species. To identify which of these transition metals were most responsible for the catalysis, XRF analysis was carried out for two ash types: NBS fly ash — only sparingly active toward S(IV) oxidation, and type D — catalytically active. Results are displayed in Table II. Surprisingly, the inactive ash contains a greater concentration of all 5 catalysts in the dry matter. Therefore the bulk metal content is not a good measure of catalytic reactivity. More important is the metal solubility, which could vary widely among ash types as it depends upon both chemical state and location in the ash particle (i.e., surface or matrix). Because the catalysis by fly ash depends on metal dissolution, leaching studies were deemed more relevant to this work.

Manganese and iron are the two catalysts present in reaction slurries at concentrations high enough to dominate the reaction rate. Theis and Wirth⁹ found that leaching with hydroxylamine hydrochloride at pH 3 removed most of the soluble Mn, leaving (on average) all but 2% of the total Fe undissolved. We used this treatment to determine which of the two catalysts — Fe or Mn — controls the reaction. Table III confirms that the hydroxylamine wash more selectively removes the extractable Mn. In addition, an interesting difference between the catalytically active (D) and catalytically inactive (NBS) ash is detected: the NBS ash contains only 1/10 the amount of soluble Mn that the catalytically active ash does. Inspection of Tables II and III reveals that

much of the Mn in the NBS ash is in an insoluble form, either a higher oxide or an interstitial cation in the aluminosilicate matrix.

Because of the nonuniformity of fly ash, we felt it important to involve several ash types in relating rates to any specific ash property. In Table IV Mn and Fe content of filtered reaction slurries and hydroxylamine extracts are compared to reaction rates. Although the $\text{NH}_2\text{OH}\cdot\text{HCl}$ treatment did affect ash reactivity, reducing it by a factor of 5-10, the correlation between reactivity and Mn content of solutions is not good. Fe concentration shows a much better correlation with reaction rates. As the hydroxylamine wash was intended to remove Mn selectively, these results seem contradictory: if the $\text{NH}_2\text{OH}\cdot\text{HCl}$ wash reduces ash reactivity, the implication is that Mn and not Fe is the responsible catalyst.

The contradiction is easily explained if one considers the following: iron in the ash is quite insoluble. It occurs predominantly in the fly ash matrix, rather than in an easily leached surface site.¹⁰ A small amount of Fe must be easily and rapidly leached from the ash, as it is found in both the filtered reaction slurries and the $\text{NH}_2\text{OH}\cdot\text{HCl}$ wash. It is entirely possible that a small fraction of the total Fe is present in a soluble form — perhaps as a surface-associated ferrous or ferric salt. The fact that the reaction reaches its maximum rate within 3-4 minutes of initiation indicates that the species responsible for the catalysis is rapidly leached from the ash. Although a higher oxide such as Fe_2O_3 should not be reduced by the $\text{NH}_2\text{OH}\cdot\text{HCl}$ wash at pH 3, it is likely that the small fraction of Fe which is readily soluble is catalytically important. In support of this hypothesis, it was found that removing Fe from solution reduced the reaction rate. By increasing the pH of reaction slurry filtrates to pH 4.5, a rust-colored precipitate ($\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}_x$) formed, which was filtered off. The freshly filtered solutions

had significantly lower catalytic activity.

In a further set of experiments we hoped to increase the Fe concentration, thereby augmenting the reaction rate. Unfortunately, stirring reaction slurries over long time periods -- doubling the Mn and Fe concentrations -- did not always increase the reaction rate. Graefe et al.² also observed this phenomenon. Further, there was not a simple relation between fly ash concentration and reaction rate: although increasing the ash content in reaction slurries generally accelerated the reaction, the rate dependence on fly ash concentration was not monotonically increasing and not reproducible with varying reaction conditions. Equilibrium control of metal dissolution could be responsible for this behavior. For instance, depending on concentrations involved and ionic strength, Fe^{3+} can maintain an equilibrium with ferric hydroxide at pH 3. This would be independent of kinetic control of the leaching described in the preceding paragraph. Chemical kinetic saturation is another possibility. Hudson found a zeroth order dependence on Fe concentration for $[\text{Fe}] > 1 \text{ ppm}$.¹¹

pH studies. The pH of the reaction mixture is important in at least two respects. Metal release is strongly pH dependent; and the relative fractions of $\text{SO}_2 \cdot \text{H}_2\text{O}$, HSO_3^- , and SO_3^{2-} are functions of pH. Many studies implicate SO_3^{2-} as the reactive species in catalytic oxidation of S(IV).^{12,13} The tendency toward enhanced metal solubility yet lower $[\text{SO}_3^{2-}]$ as pH is decreased provides opposing driving forces in the reaction.

pH dependence of the reaction was studied to see which, if either, of the two factors dominates. Control of pH is difficult in this system because buffers are complexing agents and can inhibit the reaction. No loss of S(IV) was observed when phosphate or acetate buffers were used in the reaction system. Rather than trying to discover a buffer which might not inhibit the

reaction, we used bisulfite- $\text{SO}_2 \cdot \text{H}_2\text{O}$ buffers. This necessitates working at high S(IV) concentrations and monitoring only a small fractional loss of S(IV) in order to keep the pH drop minimal (about 0.05 pH units). A study of the pH dependence of the reaction verified that opposing factors control the rate. The reaction rate increased as the pH was either raised or lowered from the rate minimum at pH = 3.

ESCA studies. ESCA studies were undertaken to determine the chemical state of metals on the ash. It was anticipated that such information for Fe and Mn could be combined with results discussed above. Unfortunately, because of instrumental insensitivity, Mn could not be detected on any of the fly ash surfaces. The Fe spectrum (Fig. 2) was easily recorded. Of the standards to which it was compared — Fe_2O_3 , $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , and Fe_3O_4 , the Fe spectrum was most similar to the Fe_2O_3 standard. We make this assignment with caution, however, because of the small chemical shifts involved and broadness of the fly ash peaks. The soluble Fe can be calculated from Tables II and III to represent less than 1% of the bulk Fe, a quantity not distinguishable on the ash surface. Other methods, e.g., scanning electron microscopy as applied by Hulett and Weinberger,¹⁴ may prove more fruitful here.

Inhibition. The presence of inorganic arsenite and SO_4^{2-} from the ash could inhibit the reaction.^{12,15} Several organic compounds also inhibit the oxidation.^{11,16} It was suspected that the NBS ash could be unreactive because of the presence of inhibitor in addition to the lack of catalyst. XRF and combustion data show the NBS ash contains more carbon and arsenic than active ash type D. Inspection of Fig. 3 shows that the NBS ash does indeed serve as an inhibitor. The time period between addition of the NBS ash and noticeable inhibition is presumably required to leach the inhibitor from the NBS ash. Extracting the NBS ash in base to remove suspected inhibitors arsenite and

cyanide does not, however, render this ash more catalytically active. In addition, neither soxhlet extraction using methanol nor combustion to remove all organic matter causes a significant rate increase.

Comparison with known rates. Attempts were made to correlate reaction rates observed here with literature values for metal-assisted S(IV) oxidation.^{13,17-22} Initial rates of the fly ash reaction were compared to initial rates calculated from the referenced equations. For each case, the concentration of metal catalyst used was the maximum found in a fly ash solution. As expected, Mn is not present in sufficiently high concentrations to account for the observed rate, whereas Fe is. Such comparisons can only be used as supportive evidence to implicate Fe in the catalysis for several reasons:

1. The S(IV) literature is not internally consistent: large discrepancies in observed rate laws exist.
2. Using fly ash, we naturally found it impossible to match ionic strength and pH values used in other experiments.
3. Synergistic effects, such as those observed between Mn and Fe by Barrie and Georgii,¹⁷ urge caution in comparisons of rates studied in single-metal systems. More study of multi-metal systems is needed if fly ash slurries are to be understood.
4. It is suspected that the iron catalysis occurs on the surfaces of hydrated ferric oxides.²² Formation of these ferric precipitates would be a complex function of the ions present in solution, thus impossible to control in fly ash systems.
5. Inhibition, which may be caused by several components present in the ash mixture, further complicates rate interpretations.

Conclusion

Fly ash is not a uniform substance. Compositional inhomogeneities are to be expected even within one sample lot. For this reason, a thorough rate study of fly ash catalyzed SO_2 oxidation was not our intent. The goal of this study has been to isolate fly ash components essential to SO_2 oxidation. Evidence presented here discounts the importance of the ash surface in this catalysis. Filtering the reaction slurry leaves the rate unchanged. Also, leaching under relatively mild conditions which should not change surface morphology renders the ash catalytically inactive. Unimportance of the ash surface is not surprising considering the low surface area ($1\text{--}30 \text{ m}^2/\text{gm}$) of most fly ash.

There are many factors which do influence fly ash reactivity: the pH range affects the distribution of S(IV) species, metal solubility, and formation of hydrated ferric oxides. Compounds which can complex trace metals or quench free radicals²¹ inhibit the reaction. The type, quantity, and chemical state of metal ions in solution all govern the reaction. Although mechanisms have been proposed for homogeneous catalysis in S(IV) solutions containing one or two different metal ions, they are not easily applied to this system. Because trace metal content varies widely among different ashes, we do not believe that it would be fruitful to propose a more detailed reaction mechanism, as such a mechanism would not likely be universally applicable. From our work, it appears that Fe plays a more important role than Mn in the oxidation; because Mn is more soluble than Fe at pH levels found in droplets and wet scrubbers, this result is important.

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Table I. Comparison of the catalytic activity of different ash types.

Ash type	Rate measured using iodometric technique ^a	Rate measured by O ₂ uptake ^b
NBS	No reaction	1.92×10^{-5}
A	5.5×10^{-5}	12.0×10^{-5}
B	5.8×10^{-5}	3.6×10^{-5}
C	6.2×10^{-5}	8.0×10^{-5}
D	5.0×10^{-5}	6.8×10^{-5}

^a-d[S(IV)]/dt, moles/l·min - zeroth order rate

^bConverted to -d[S(IV)]/dt, moles/l·min

Table II. XRF comparison of type D and NBS ash.

Element	Concentration (ppm)	
	"D" ash	NBS ash
Mn	200 ± 50	510 ± 70
Fe	$25,000 \pm 2000$	$62,000 \pm 6000$
V	<200	<200
Co	<150	<150
Cu	65 ± 9	140 ± 10

Figure Captions

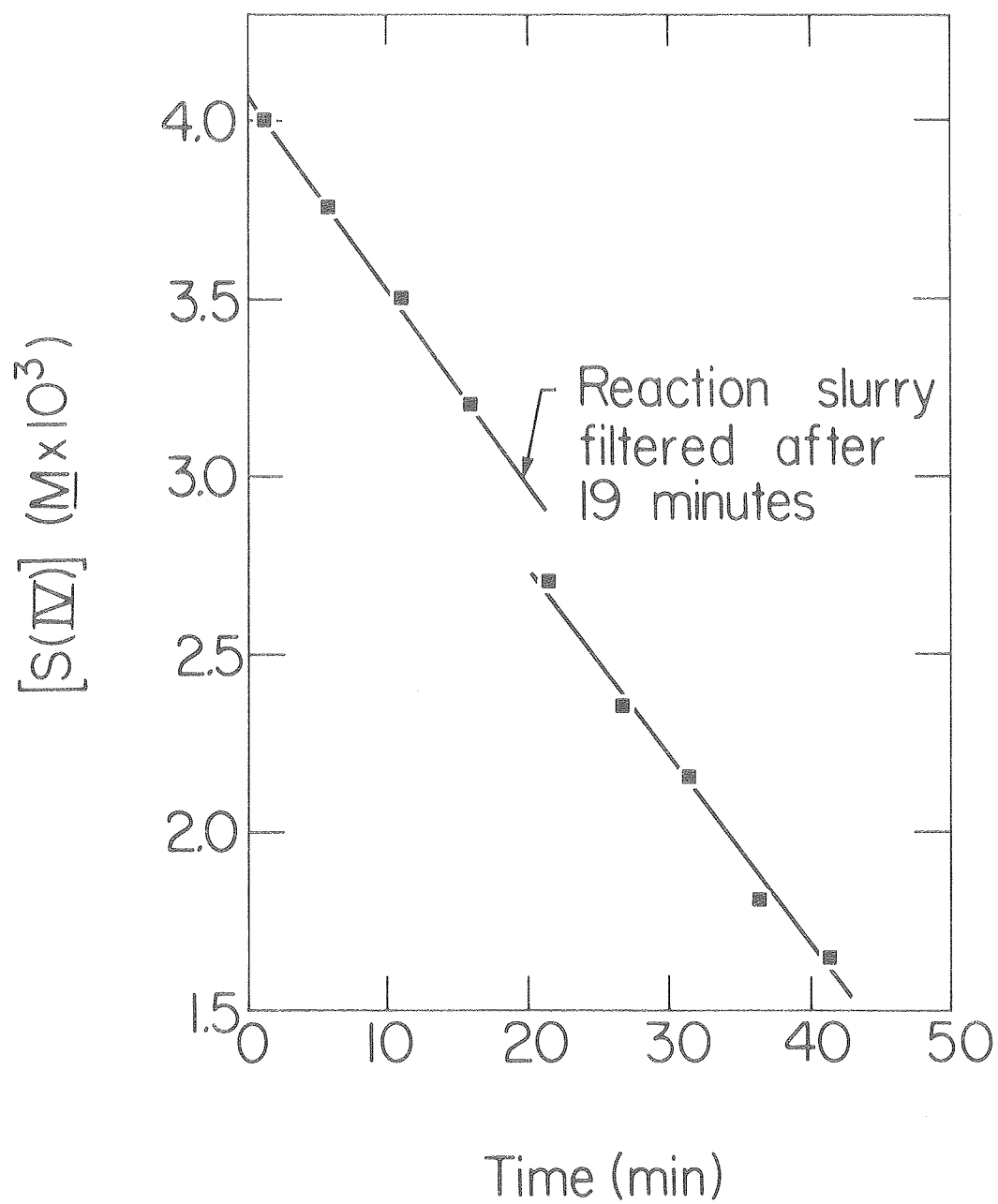
Figure 1. Comparison of rate of [S(IV)] oxidation before and after filtering

reaction slurry. Initial pH = 2.9, ["D" ash] = 0.18%.

Figure 2. ESCA spectra of fly ash showing Fe(2p) region and C(1s) reference.

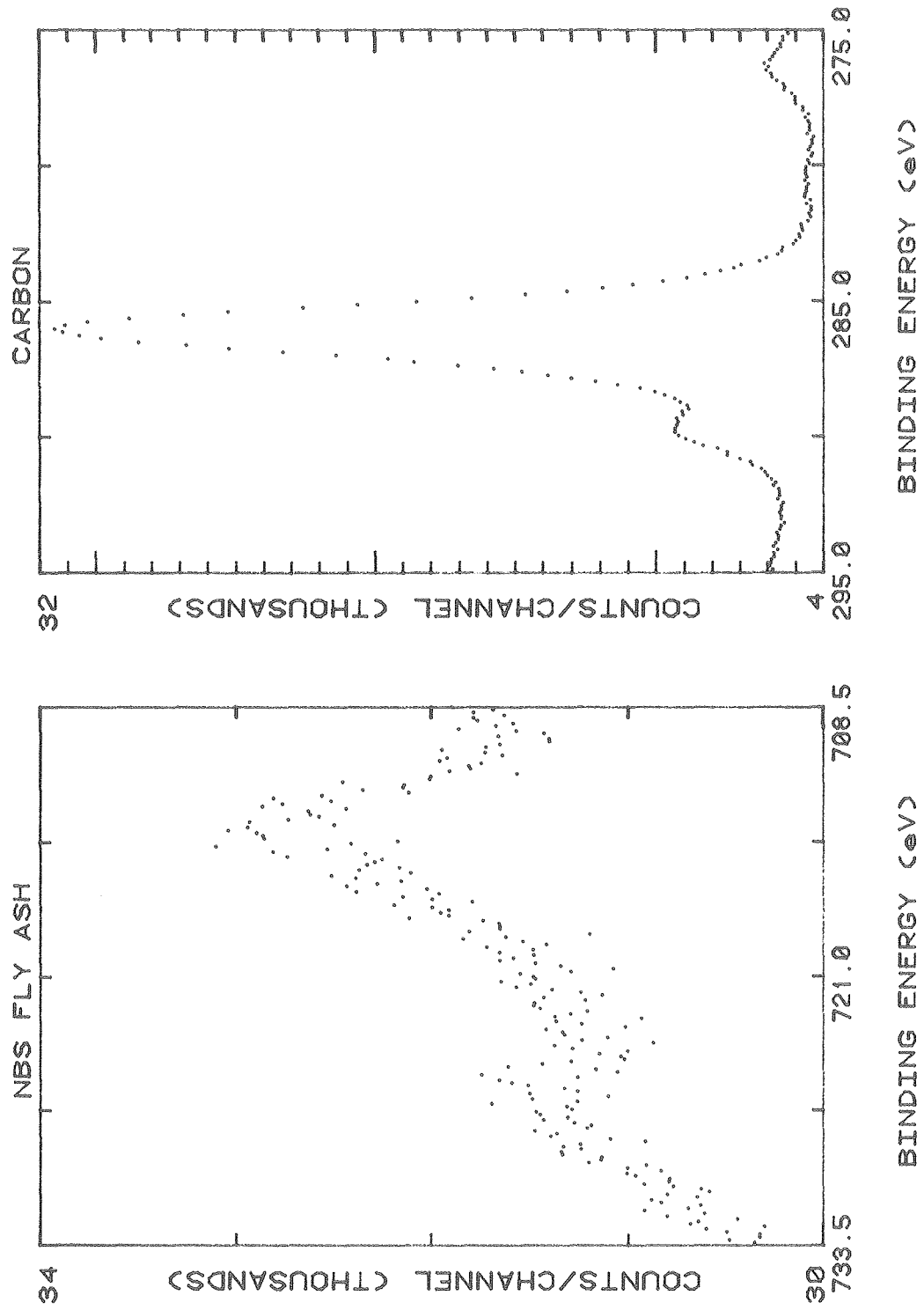
Figure 3. Demonstration of rate inhibition by NBS ash. Initial pH = 2.9

± 0.1 , ["D" fly ash] = 0.15%.



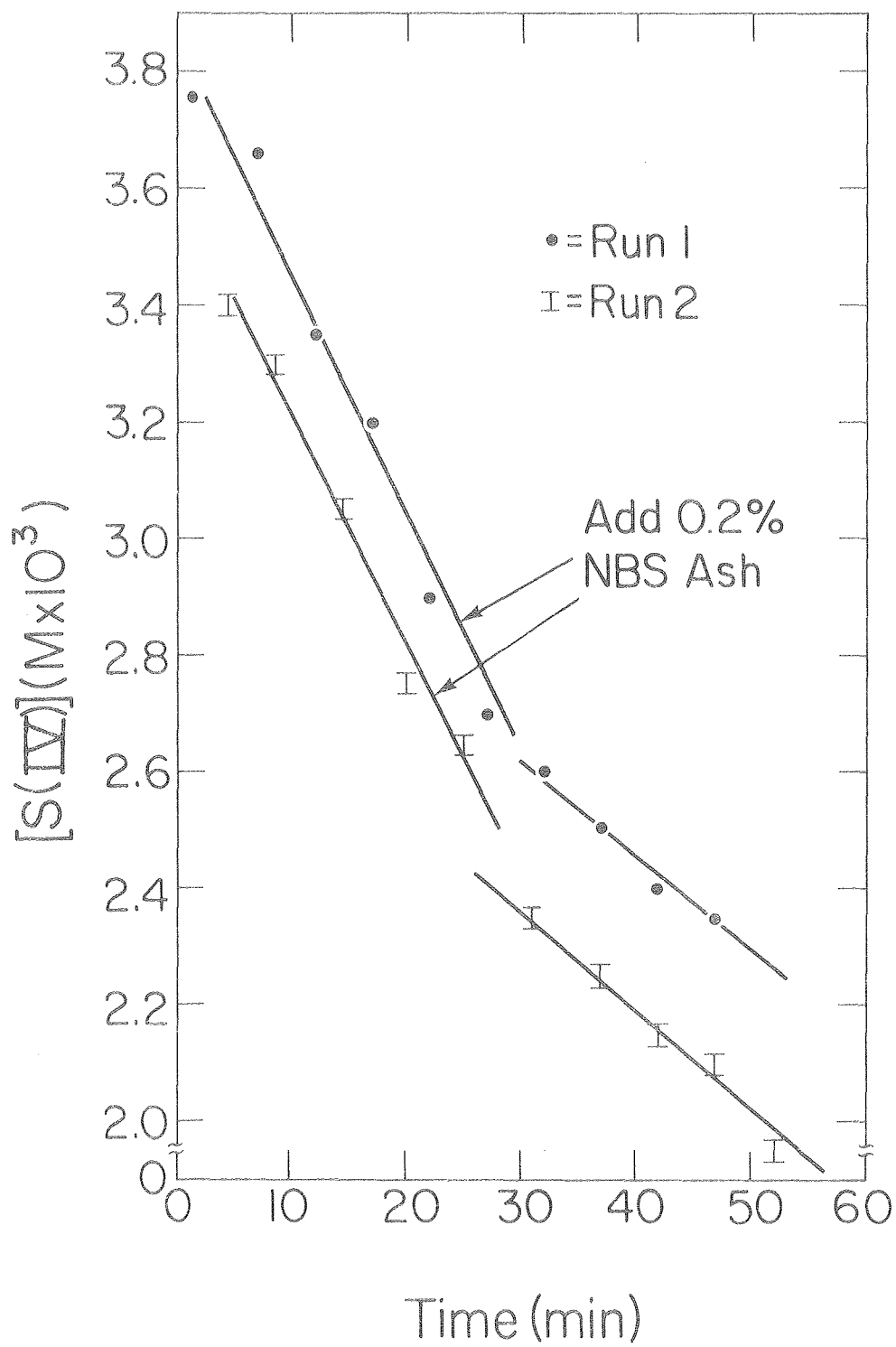
XBL 809-1927

Figure 1



XBL 8011-3934

Figure 2



XBL 809-1926

Figure 3

